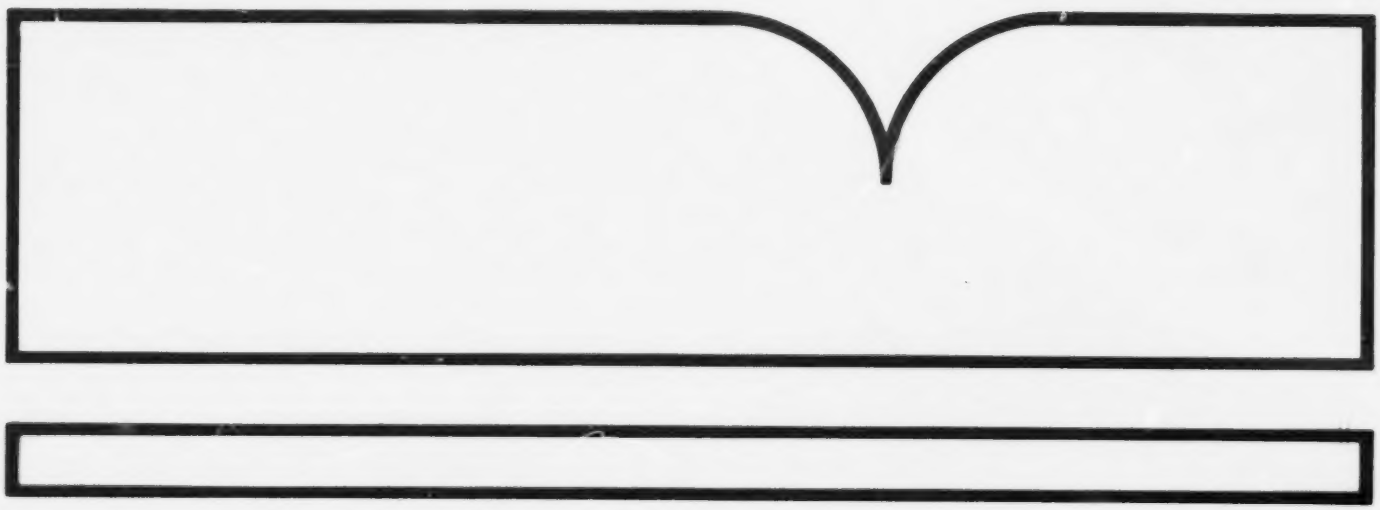
PB80-177801

Fate of Toxic Organic Substances in the Aquatic Environment

(U.S.) Environmental Research Lab.
Athens, GA

1978



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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/J-78-164	2. JOURNAL ARTICLE	3. RECIP PB80-177801
4. TITLE AND SUBTITLE Fate of Toxic Organic Substances in the Aquatic Environment		5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Ray R. Lassiter, George L. Baughman, and Lawrence A. Burns		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens, Georgia 30605		10. PROGRAM ELEMENT NO. A1VL1A 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Athens GA Environmental Research Laboratory College Station Road Athens, Georgia 30605		13. TYPE OF REPORT AND PERIOD COVERED Chapter in Proceedings 14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES IN: State-of-the-Art in Ecological Modelling. Vol.7. S.E. Jorgensen (ed.). International Society for Ecological Modelling. Copenhagen, Denmark. 1978. p.219-246. Contact: R.R. Lassiter, 250-3103

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Environmental Simulators Mathematical Models		12A 68D

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NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/J-78-164
JOURNAL ARTICLE

State-of-the-Art in Ecological Modelling. Vol. 7. 219-246,1978

FATE OF TOXIC ORGANIC SUBSTANCES IN THE AQUATIC ENVIRONMENT

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ABSTRACT

Models that predict the environmental fate of toxic chemicals can be used as guides for data acquisition for currently used chemicals and as tools for calculating expected environmental concentrations of new chemicals introduced into commerce. These models are based on a set of mathematical descriptions of rate processes of chemical transformations and equilibria, both written as functions of environmental factors. To test the model, it must be used to make predictions that can be observed experimentally. For the tests, experimental environments should be employed that can be controlled to provide the conditions for which the predictions were made. Application of the models requires that a file of environmental descriptions be available. Several applications have been made.

FATE OF TOXIC ORGANIC SUBSTANCES IN THE AQUATIC ENVIRONMENT

The conflict between enhancement of the quality of life through the use of new chemicals and the simultaneous need to minimize their potential hazard is a contemporary dilemma. The paradoxical ease of obtaining any single unit of information about a chemical and the contrasting difficulty of extrapolating the information to potential hazard heightens this dilemma.

A rational and systematic means of assessing environmental hazard would fill a critical and long-standing need, a need recognized by the U.S. Congress in its passage of the Toxic Substances Control Act (PL 94-469). This legislation greatly increases the number of chemicals subject to control and mandates the development of test protocols for generating data on which to base regulatory decisions. The need for a data analysis rationale to precede protocol development is implicit in this mandate. Requirements for data collection must be based on a rational and systematic scheme for evaluating the behavior of chemicals in the environment. Use of a system model appears to be a feasible means of analyzing chemical data, and therefore a useful guide for data acquisition. Suggestions that mathematical models (1-5) be used for exposure prediction are not new. Unfortunately, the problem of <u>how</u> this

could be done has not been addressed. Instead, most authors have concentrated on identifying the factors influencing the environmental concentration and fate of pollutants.

EXPOSURE ASSESSMENT: THE NEED AND THE PROBLEM

"Many expensive decisions relating to the impact of environmental pollution on public health and welfare are based on meager and sometimes unreliable scientific data. Consequently, choices are made between different opinions rather than by selection of the best alternative." (1). This statement illustrates a misconception that seriously impedes our ability to make environmental decisions. It implies that "selection" among alternatives is a scientific process, when in fact "best" is a value judgment that, unless operationally defined in terms of some quantitative measure, cannot be treated objectively. Decisions are based upon a wide variety of information, much of which is difficult to quantify. Therefore, decision-making in the face of uncertainty will continue. Thus, it is prudent to seek ways to make rational judgments using data that may seem "meager" and "unreliable" to both the scientist and the decision maker. Lacking such a rationale, we must postpone decisions until definitive information is available or make decisions based upon arbitrary and poorly specified criteria containing unrecognized value judgments. Value judgments "can not and should not be avoided, but they should be made explicit and not introduced in so intellectually muddled a way that no one knows which are the

facts and which the judgments" (6).

Assessment of ecological impact or evaluation of hazard posed by a toxic chemical can be approached in many ways. All approaches share the need for a method to estimate exposure (the ambient concentration of a pollutant and the expected nature and duration of the contact between organism and toxicant). Here we face the problems and potentials of estimating concentrations of organic chemicals that have either been used but not measured in the environment or that have not yet been introduced into the environment. Although environmental concentrations are only part of the information required for evaluation of overall hazard, they are necessary for rational decision-making.

Environmental scientists generally agree that the "fate" of pollutants is an important part of the body of information required to assess environmental impact and distribution. Too frequently, however, fate has been equated to an observed spatial distribution and not necessarily to concentrations, nor to the factors responsible for distribution. Historically, the way we viewed "environmental problems" was heavily influenced by rapid developments in residue analysis and the resulting growth of information on the distribution of pesticides. Another, and perhaps equally important, factor has been the notion that processes occurring in aquatic systems are dominated by the activity of biological communities and are therefore too complicated to understand (7). These views lead

to assumptions that transformations in water and soil are wholly microbial (8) (neither physical nor chemical) and that the application of basic science and scientific method to the quantification of environmental processes would constitute puerile reductionism (9), unreliable in environmental studies. It is understandable, therefore, that attempts to explain the influence of environmental processes on the impact and distribution of chemicals have frequently been considered hopeless or impractical. This opinion is now subject to critical reassessment in light of recent research elucidating the nature of many transport and transformation processes (12-15). Much progress has been made, particularly with respect to processes such as metal complexation (11), kinetics of chemical and photochemical transformation of organics (12), and volatilization (13-15).

The development of a high level of understanding of processes, the contrasting poor capability to utilize the process information for general environmental assessments, and the increasing need to make these assessments has led to applications to special cases (15-17) and a few approaches toward generalization (3,4,18,19). Potentially, the environmental behavior of a large number of chemicals must be assessed. Many of these chemicals may be introduced to a wide variety of environments. This situation results in a very large problem for which to design a generalized assessment tool. It is recognized (5,20) that expected environmental

concentrations are needed for overall hazard assessment, but little has been written on the environments for which the concentrations should be calculated. Smith et al. (18,19) and Baughman and Lassiter (3) discuss some simplified descriptions of aquatic ecosystems. Environmental descriptors that retain salient features of ecosystem variability at a useful level of resolution are a subject of current research.

BASIS FOR A COMPUTATIONAL MODEL

Development of a conceptual framework to predict net environmental behavior of a chemical is, admittedly, a speculative endeavor. This is in keeping with the historical development of modern science (21,22). In spite of warnings that it will be a fruitless exercise, we see as a natural step, the synthesis of current understanding of transport and transformation processes into a rationale that explains distribution, products, and concentration via kinetic competition among processes conditioned by characteristics of the environment.

Our calculations are based on conservation of mass as an organizing principle, and we postulate a set of causal mechanisms that remove a chemical from the environment into which it is introduced. The hypothesized set of removal mechanisms and the underlying assumptions are testable in a variety of contexts. We shall use the term 'rationale' to mean the formalized idea that environmental concentrations of toxic

organic substances (TOS) can be calculated and include in this meaning the selected relationships and empirical observations that we use to develop the idea. The term 'model' is used for the calculational instrument that embodies the rationale and which is tainted with the compromises of the real world for the sake of utility.

Because the "predictions" will in general be made for archetypal environments, these models perhaps should not be termed "predictive" in the usual sense. Rather they will be called "evaluative" models because the results will be used to evaluate probable levels of a selected chemical in typical environments. The set of predictions over the range of environments corresponding to environments typical of those that would potentially receive the chemical would form a prognosis of the "environmental behavior" of the chemical.

In general the dynamics of a TOS in the environment can be represented as a sum of contributing processes, such that

$$-\frac{dS}{dt} = V + P_D + P_S + H + A + M \pm Se + D - L$$

where S is the quantity or concentration of the TOS in the system and the process list includes volatilization (V), direct photolysis (P_D), sensitized photolysis (P_S), hydrolysis (H), breakdown by photo-autotrophs (A), microbial degradation (M), exchanges with sediment reservoirs (Se), dilution (D), and loadings of TOS into the system (L).

This formulation assumes that the toxicant is present at low concentrations that do not affect the operation of removal

mechanisms. By this assumption the properties of the system are independent of the pollutant and can be considered external variables (or constants). If this assumption does not hold, the rationale must encompass as state variables all the environmental features that are affected by the pollutant. In the limit, prediction of the fate of a pollutant would require that the computations encompass every time-varying feature of the affected ecosystem. It is much more convenient, therefore, and probably correct to a high degree of resolution, to ignore possible effects on removal mechanisms.

Analytical and computational advantages permit formulation of the problem so that a formal evaluation of dispersive fluxes can be neglected. In analysis of riverine systems, for example, it is usually assumed that advective flows so dominate dispersion that the latter can be ignored without serious consequence. Dispersive fluxes within a lake or within sediment zones, however, are of some significance to the fate of TOS. Use of compartments and compartmental analysis to represent physically separable elements of the environment requires arbitrary boundaries but allows substitution of ordinary differential equations for the considerably less tractable partial differential equations. Dispersive fluxes can be represented by simple mass exchanges among compartments, and thus it is possible to preserve important features of, for example, sediment storage of TOS with a significant gain in computational facility. Any "compartment" (i.e., physically

homogeneous element) of the aquatic ecosystem can be represented as a particular volume containing water, particulate material, biota, dissolved materials, etc. Loadings and exports are then represented as mass fluxes across the boundaries of the volume element (processes Se, D, and L), whereas reactive properties are treated as point processes centered within the volume.

Equilibria

Processes that distribute the TOS among various forms (but do not result in removal of TOS from the systems) usually occur very rapidly (relative to transport and degradation). These processes are represented by equilibrium calculations. The distribution coefficient for the i^{th} form, α_i, times the total, S_T, gives the concentration of the i^{th} form. Currently, dissociation into charged species, sorption onto particulate material, and ion exchange are represented as equilibria. Cases for which sorption or dissociation could be better represented kinetically probably exist as well. To illustrate the derivation and use of distribution coefficients, the simplest example including dissociation, sorption, and ion exchange is given. The three chemical equations for these processes are

$$S + H^+ \rightleftharpoons SH^+, \quad K = [SH^+]/([S][H^+])$$

$$S + P \rightleftharpoons SP, \quad K_p = [SP]/([S][P])$$

$$SH^+ + P \rightleftharpoons SP^+, \quad K_+ = [SP^+]/([SH^+][P]),$$

where the neutral dissolved form of the pollutant (S) is

subject to protonation (H^+) and both (S) and the protonated species (SH^+) are subject to sorption by particulate materials (P) to give (SP) and (SP^+) respectively. Referral of all concentrations to the aqueous volume of the system and expression of (P) as (kg/l) leads to conventional units for the equilibrium and partition coefficients (K, K_p, and K_+). The sum of the concentrations of the forms equals the concentration total, S_T:

$$S_T = [S] + [SH^+] + [SP] + [SP^+].$$

These four algebraic equations can be solved for the four unknowns as ratios to the total concentration, S_T. These ratios are the distribution coefficients, α_i. For example, $\alpha_o = ([S]/ S_T) = (1 + K [H^+] + K_p [P] + KK_+ [H^+][P])^{-1}$ is the fraction existing in the uncharged, dissolved form.

Removal Processes

A TOS released into the aquatic environment will be subject to physical, chemical, and biological processes whose rates of reaction and governing mechanisms can be determined by laboratory bench studies. These include photolysis, volatilization, hydrolysis reactions, and photo-autotrophic and heterotrophic microbial degradation. For TOS that protonate and/or sorb, reaction terms include the appropriate distribution coefficients (α_i).

Volatilization

Losses of the TOS across the air-water interface are

controlled by the vapor pressure of the TOS and mixing characteristics of the water body. The most convenient, and probably most accurate, means of modeling volatilization of a TOS in flowing waters has been described by Tsivoglou (23) and applied in an analysis of vinyl chloride by Hill et al. (15). In this method the volatilization rate of the TOS is referred to the reoxygenation rate of the water body (k_2), with the latter (a much-studied quantity) accounting for the mixing properties of the system. Although the exchange rates will change with variations in turbulence, etc., the ratio of exchange rates, TOS:O_2, will not. The property of the TOS requiring laboratory identification then reduces to a simple parameter (k_v) relating volatility of the TOS to reaeration, and volatilization (V) can be represented as

$$V = k_v k_2 \alpha_o S_T$$

where α_o is used to account for the fact that only the uncharged, dissolved form volatilizes.

This procedure has not been shown to hold for non-flowing water bodies, and in addition, reaeration rates are less widely available for these systems. Mackay and Leinonen (14) have developed an expression based upon assumed exchange of gases across the air-water interface through stagnant films. This expression is applicable to non-flowing water bodies:

$$V = \frac{A}{Vol} \left(\frac{1}{k_L} + \frac{RT}{K_H k_G}\right)^{-1}$$

where A is interfacial area, Vol is volume of the water body, k_L is exchange rate coefficient through the liquid film, R is the gas law constant, T is absolute temperature, K_H is the Henry's law constant, and k_G is the exchange rate coefficient through the gas film.

This formulation reduces to simpler forms for extreme environmental conditions.

Direct Photolysis

Direct photolysis rates of TOS can be reduced to a simple dependence on ambient light intensity and concentration of reactive species via laboratory studies of the absorption spectrum and quantum yields of the material. Assuming that the water column is well mixed (either to the bottom or to some other appropriate depth), direct photolysis can be expressed as

$$P_D = \Phi I \Sigma k_{di} \alpha_i S_T$$

where Φ is quantum yield for the reaction, k_{di} is a function of absorption properties of the TOS, I is average sunlight intensity in the water column, and the values of i (in $\Sigma\alpha_i$) indicate the reactive species of the TOS in this process. Given the light intensity at the water surface (I_o), the average intensity within the water column can be calculated as a property of the amount of suspended solids and colored substance in the water.

Sensitized Photolysis

TOS are also subject to light-mediated chemical reactions

in the presence of naturally occurring organic materials (e.g., humic and fulvic acids). The reaction pathway appears to proceed by light-activation of humic compounds, which in turn react with the TOS. Assuming that the TOS is present only in trace amounts, consumption of the sensitizing material (S_s) can be neglected and the process can be regarded as a second order reaction. The reaction can then be represented as

$$P_S = \Sigma k_{si} \alpha_i S_T S_s$$

where k_{si} is a rate coefficient and S_s is concentration of sensitizing material.

A competing reaction involving photo-activated humic material and molecular oxygen produces singlet oxygen. Significant retardation of rates of P_S are likely to occur as a function of dissolved oxygen concentration in natural waters (24).

Hydrolysis

Hydrolytic reactions of TOS are generally of three types: reactions involving water, acid and base. Given $[H^+]$ and $[OH^-]$ the reaction rate can be represented generally as

$$H = \{[H^+]\Sigma k_{ai} \alpha_i + \Sigma k_{wj} \alpha_j + [OH^-]\Sigma k_{bl} \alpha_l\} S_T$$

Ionized species can undergo hydrolysis reactions at differing rates, so the rate coefficients will require separate laboratory determinations for each species when these are present.

Biolysis

Biological degradation is a major breakdown pathway for

many toxic substances. This parameter is frequently estimated by selective enrichment studies using the compound of interest as a sole carbon source (18). However, the competitive ability and population densities of such populations may well be unobtainable for real ecosystems. A significant need exists for rate coefficients (and experimental protocols) that can be formulated in terms that include environmental parameters that influence the biolysis rate. Biological transformations of TOS can be conveniently subdivided according to the energy consuming pathway involved: microbial heterotrophic or photo-autotrophic.

Photo-autotrophic Degradation (A) --

Although little quantitative work has been done to establish the general importance of the phenomenon, some TOS are degraded at significant rates by photosynthetically active green plants (25). For example, methoxychlor can be degraded at significant rates by algal populations under illuminated conditions (29). At present we hypothesize that TOS degradation can be correlated with gross or net primary productivity of an ecosystem. Productivity of ecosystems has been fairly well characterized, so this parameter could provide a means of translating laboratory rates into rates applicable to various environments. A possible functional representation is

$$A = \Sigma k_{ai} a_i S_m P$$

where k_A is the second order rate coefficient and P is productivity in the laboratory or field. Relative to other processes described here this process is of questionable general importance. Several other processes could be postulated in the same manner, and one possible outcome of testing is to identify some of these important processes.

Microbial Heterotrophic Degradation (M) --

When studies of TOS degradation by mixed bacterial populations are available, this process can be represented as

$$M = \Sigma k_{Bi} \alpha_i S_T B$$

where α_i accounts for the degradable fraction of TOS, B is microbial activity (by some convenient measure such as population density in cells ml^{-1}), and k_B is a second-order rate coefficient (ml $cell^{-1}$ hr^{-1}).

This is a simpler relation than is often assumed for bacterial decomposition, but it has been shown to be sufficient for some cases (26). Monod kinetics have seen frequent use, but at trace (i.e., environmentally significant) concentrations of TOS, microbial decomposition rates should be linearly proportional to concentration.

VALIDATION

Caswell (27) discussed two purposes that systems models serve--understanding and prediction. Models for understanding are theoretical models and in many cases have the properties

that we ascribe to theories. In fact they are not theories, but rather are instruments for application of theory. Predictive models are constructed in any way that attains an acceptable level of predictability over a useful range of application. As Caswell notes, predictive models are often composed of terms that are only indirectly related to causal factors in the real world. They are validated when shown to be useful for their intended purpose. Theoretical models are built of expressions supposed to be direct mathematical descriptors of the way the real world operates. These expressions are independently tested and correspondingly relatively well-founded assumptions of the model.

Theoretical models are also required to make predictions, and in fact only theoretical models are capable of making secure predictions outside their range of prior observation. To test a theory one uses the model to make predictions and then examines the corresponding real world case to determine whether the predictions are confirmed. For environmental models the kinds of predictions that are required have often been unclear, and identification of critical predictions for testing has been difficult. Many environmental models have been "calibrated," that is, their parameters have been adjusted so that they match certain data well enough for some purpose. Tests that present little opportunity for rejecting the model have often been used. For example, a data set may be divided into two parts (perhaps from two years of field data). The

parameters are fitted ("calibrated") using one portion of the data, and the model is asked to "predict" the other portion ("test"). This kind of test is subject to the statistical objection that it will too often fail to reject fallacious models, and thus may lead to exaggerated confidence in the models and in their results.

For a definitive test, a falsifiable hypothesis must be formed consisting of clearly recognizable predictions, preferably including alternative hypotheses as with Platt's "strong inference" (28). For cases in which this is not possible, differences between observed and predicted results can be evaluated statistically. Failure to observe the predicted phenomena provides grounds for rejection of the model. Observations that do not differ significantly from the predicted results provide grounds sufficient to continue working with the model, though not to prove it correct.

Brockway et al. (29) described a critical test of a model (actually of the underlying rationale) used to predict the fate of methoxychlor. In this case a laboratory microcosm was used as the test environment. Based upon a loading rate into the microcosm, which was an open system, and a postulated set of transformations, a steady state concentration was calculated. In replicate systems the actual concentrations were far from the predicted and the hypothesis that the rationale was complete was rejected. Another process, unaccounted for in the original model, was found to be operating at a significant rate.

This test illustrates two important aspects of testing environmental models. First, studying a natural environment is not always the wisest choice when a critical test is attempted. In natural ecosystems variation resulting from uncontrolled environmental fluctuations can make real differences undetectable. Laboratory ecosystems that are maintained in controlled environments can provide a better opportunity to detect an incomplete or improperly described set of transformations. Tests in the natural environment are useful to quantify the effects of temporal and spatial aggregation of environmental descriptors.

The second important point illustrated by the methoxychlor case is the proper sequel to rejection of a model. An environmental system model consists of representations of many simultaneous and serial processes. After rejection, therefore, one seeks the specific misrepresentations or inadequacies of the model. In practice it will probably be clear from prior suspicions that certain processes are inadequately described, or the nature of the results will implicate some process that has been omitted from the model.

The fundamental weakness of a rationale based upon a sum of parallel processes lies in the possibility of completely omitting important but unsuspected processes. There is no way to mechanically or systematically guard against such an event. If an important process if omitted, a critical experiment will show the model to be inadequate; increased precision in

characterizing the known processes or in describing the system should fail to compensate for this kind of inadequacy. On the contrary, increased precision will highlight the inadequacy.

GENERAL APPLICATIONS

A general description of the removal of a TOS from aquatic systems can be expressed at many levels of resolution, and variations on the set of hypothesized removal mechanisms are possible. A model containing the processes described above is a component in a computerized EXposure Analysis Modeling System (EXAMS) under development in our laboratories. Smith et al. (18,19) used a subset of the set of mechanisms included in EXAMS and Branson (4) used a similar subset. Park et al. (30), however, include additional mechanisms, postulating that both decomposition catalyzed by colloidal material and by micelle-like units of humic acids could be important. The model by Park et al., PEST, is also written at a higher degree of resolution. PEST distinguishes floating from suspended particles, separates particulate materials into chemically different fractions, and includes fish uptake for several subpopulations. Models that differ in their level of resolution and removal mechanisms can be considered as directed toward different ends. When different removal mechanisms are postulated, however, qualitative differences in predicted results are possible. The models can thus be considered alternative hypotheses, and therefore stimulatory of further research and better theory after critical tests are performed.

If environmental factors (including transport) and loading rates are essentially constant over a period of interest, the equations reduce to pseudo-first-order expressions. In this case the steady-state concentrations of TOS in the compartments, $\underline{S}$, can be computed from

$$\underline{S} = [kE]^{-1} \underline{L}$$

where kE is the first-order rate constant matrix (second order rate coefficients times environmental factors) and $\underline{L}$ is the vector of loadings into the compartments.

If constant conditions cannot be assumed, then calculations will need to be made as a function of time. For example, if conditions (loadings, engineering works, etc.) along a river are expected to change with time, then the temporal pattern of environmental concentrations will be of interest.

Application of theory, however, requires more than simply writing a mathematical model. The model must be associated with other capabilities, for example, a means of selecting relevant environments and a method for calculating loading rates of TOS. Ideally a large set of environmental descriptions could be stored in a computer file, and a small set of relevant environments selected for evaluating a specific chemical. For maximum utility environments should be described in a canonical form, that is, in the simplest terms possible that permit application of the underlying chemical and ecosystem theory. The description of the reactions affecting organic pollutants guides the selection of descriptors for the

specification of environments. Chemical and biochemical transformation rates are expressed as a rate coefficient times a product of the concentrations of two reactants, one a component of the environment and the other the reactive form of the pollutant (Table 1). The environment should be specified as to the concentration (or other intensive property) of the environmental reactants, plus other relevant properties such as temperature, flow velocity, etc. The structure of EXAMS, Figure 1, includes these features.

We are not yet sure what temporal and spatial resolution is appropriate to EXAMS. The needed level of resolution of environmental detail will probably become clearer as a result of use rather than from purely theoretical considerations. Construction of the large set of canonical environments, algorithms for selection of relevant environments from the large set, and algorithms for calculating loading rates are subjects of current research.

SUMMARY

A rationale for calculating the removal of toxic organic chemicals from aquatic systems rests upon an assumption of (1) low levels of the chemical so that there is no effect on removal process mechanisms and (2) on the existence of a delimitable number of removal processes conditioned by environmental parameters. The rationale needs to be tested both for its applicability as a tool to help evaluate the hazard of toxic chemicals and for its scientific validity.

Table 1. Properties of environments and chemicals important in disappearance of chemicals from aquatic systems. (Symbols are consistent with those used in the text.)

Process	Envir.	Chem.
Volatilization	mixing	K_H
Hydrolysis	pH	k_a, k_W, k_b
Direct photolysis	I_0, P	ϕ, k_d
Sensitized photolysis	S, I_0, P	k_S
Biological degradation	M	k_B
Photoautotrophic degradation	A, I_0, P	k_A
Sorption	P, POC	K_p, K_+
Ionization	pH	K

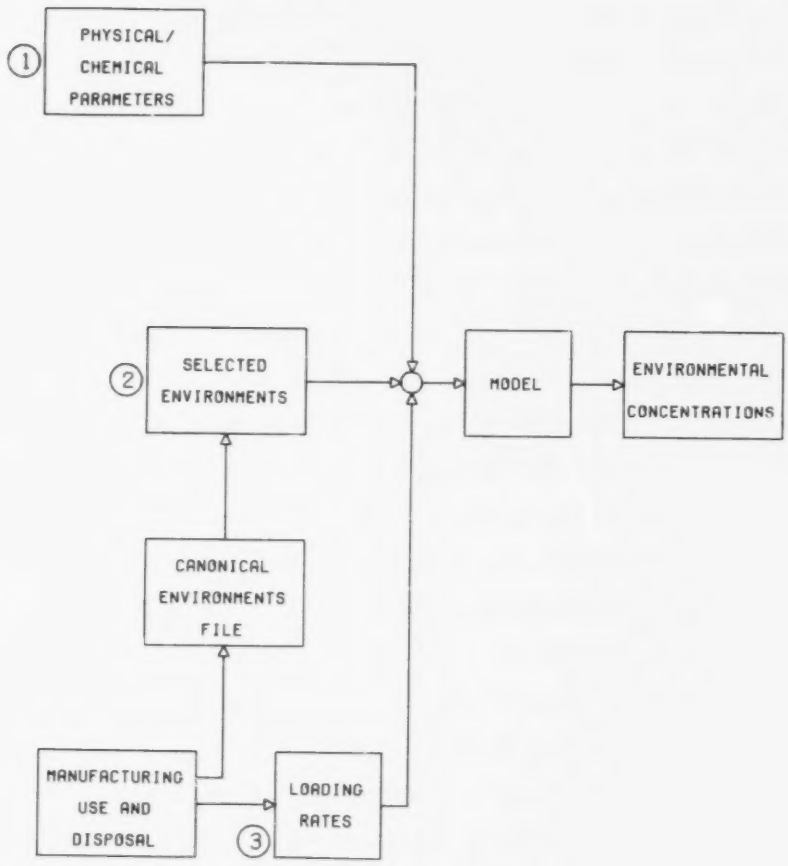

Figure 1. Structure of the EXposure Analysis Modeling System (EXAMS).

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